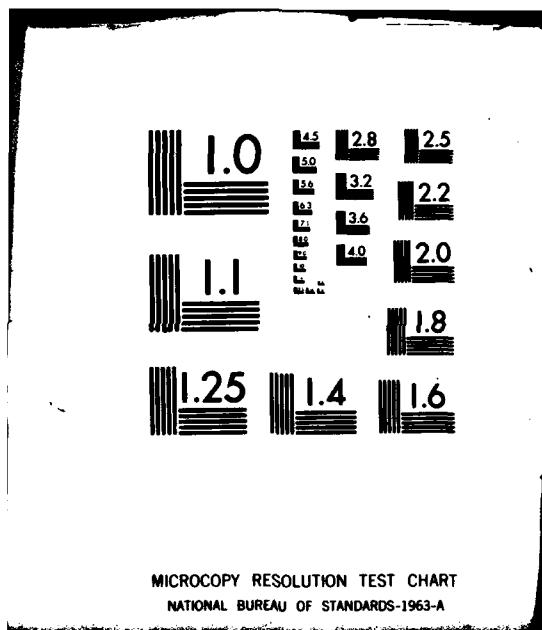


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Intrinsic Step-Related Surface State on Ir(332)

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J.F. van der Veen, D.E. Eastman and A. M. Bradshaw

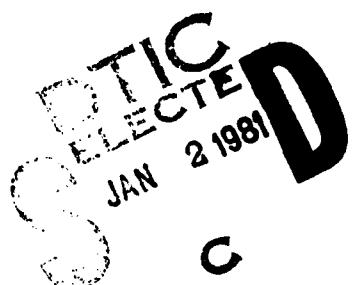
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Intrinsic Step-related Surface State on Ir(332)*

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Abstract: Using angle-resolved photoemission, we have identified a new surface state on Ir(332), which can be unambiguously associated with step sites. This state is located near the Fermi level and can be distinguished from a terrace-related state by preferential adsorption of hydrogen on the rows of step atoms. Both states have Λ_1 symmetry and are located in a relative sp-hybridization gap above the L_2' point.

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It is experimentally well established that the presence of steps on surfaces of transition metals can promote chemisorption as well as chemical reactions between adsorbed species.¹ Although the enhanced reactivity of these surfaces is thought to be related to intrinsic step-specific electronic states, to date there has been no direct experimental evidence for such features on metal surfaces. In recent photoemission experiments on stepped Cu(211)² and Au(211)³ surfaces, only a single surface state was found in the sp gap around the L point of the bulk Brillouin zone similar in nature to the one observed in normal emission from the flat Cu(111) and Au(111) surfaces. In this paper we report the first photoemission observation of a new intrinsic surface state near the Fermi energy E_F which can be unambiguously associated with the step sites on a Ir(332) surface. This step-related state could be distinguished from a second state, which is related to the (111) terraces on this surface. The latter is similar to the surface state reported for Ir(111).⁴

Both surface states have approximately Λ_1 symmetry and are located in the sp-hybridization gap around the L point. Energy dispersions $E(k)$ have been determined for these surface states. We further show that these surface states provide a new way to distinguish between catalytic reactions at step and terrace sites.

Angle-Resolved Electron Energy Distribution Curves (AREDC's) were taken with a two-dimensional display-type spectrometer⁵ at the Synchrotron Radiation Center of the University of Wisconsin. The overall system resolu-

tion (monochromator plus spectrometer) was 150 meV; the angular acceptance was $\delta\Theta \approx 3^\circ$. Single crystal Ir(332) and Ir(111) surfaces were cut ($\leq 1^\circ$ accuracy), mechanically polished, and lightly etched in aqua regia. Clean surfaces (as judged by Auger spectroscopy) were prepared by sputtering and repeated cycles of heating in oxygen at 1300 K and flashing in vacuo to 1500 K. The Low Energy Electron Diffraction (LEED) pattern of the Ir(332) surface showed doublet features characteristic of six rows of terrace atoms of (111) orientation with single layer atomic steps of (11-1) orientation at every sixth row.

Step- and terrace-related surface states on Ir(332) were identified by selective adsorption of hydrogen as shown in Fig.1. AREDC's were taken for $h\nu=10.3$ eV (mixed s/p-polarization) and parallel momentum $k_{\parallel} = 0.25\text{\AA}^{-1}$ corresponding to the \bar{Y} -point of the (332)-Surface Brillouin Zone (SBZ) (see insert of Fig.2a). For $h\nu=10.3$ eV, the \bar{Y} -point is probed at a polar emission angle which is close ($\sim 3.5^\circ$) to the direction of the (111)-terrace normal. The spectrum for the clean (332) surface shows prominent surface state emission near E_F . After exposure to 0.5 L of hydrogen, the emission intensity of E_F (cross-hatched in Fig.1) decreases drastically and continues to decrease up to an exposure of ~ 1 L. Further hydrogen exposure up to 10^3 L produced only a slight reduction in intensity of the remaining feature at 0.6 eV below E_F (single-hatched feature in Fig.1), while the LEED pattern remained (1x1). This exposure dependence can be explained as follows. The hydrogen dissoci-

atively adsorbs on the step sites until all are occupied. The observed decrease of emission intensity at E_F corresponds to the quenching of an intrinsic step-related surface state. Such preferential adsorption of hydrogen at step sites has also been observed on Pt surfaces in combined thermal desorption and work function studies⁶ as well as in electron loss spectroscopy.⁷

The prominent peak remaining after hydrogen adsorption (single-hatched feature in Fig.1) is attributed to a surface state associated with the (111)-oriented terraces, since it closely resembles a surface state found in normal emission on Ir(111)⁴ (top curve in Fig.1). Contrary to what is observed for the step-related surface state, the emission intensity of this state is only quenched by ~ 15% for hydrogen exposures as large as 10^3 L. This indicates that only a low hydrogen equilibrium coverage on the terraces was achieved under the conditions of measurement ($P_{H_2} \leq 3 \times 10^{-11}$ Torr, $T = 300-350$ K), and that hydrogen adsorbed at step sites is more strongly bound, in agreement with Ref.8. On the other hand, atomic hydrogen produced by a glowing filament near the sample caused a partial quenching of the terrace-related state and a ~ 0.1 eV shift towards higher binding energy (not shown in Fig.1).

Both surface states are completely quenched if the surface is exposed to 30 L of oxygen (Fig.1), which corresponds to the formation of a single-domain (2x1) overlayer, as found in Ref.9. The residual peak at E_F disperses with photon energy and has been shown to be due to bulk d-band emission.^{4,10}

The approximate symmetry of the surface states has been determined by polarization-dependent measurements. According to dipole selection rules for normal emission from an ideal (111) surface, only Λ_3 -symmetry initial states are allowed if the electric field vector is parallel to the surface (s-polarization).¹¹ As shown in Fig.1 for clean Ir(332), both surface states disappear for s-polarization; from this observation it is concluded that these states have Λ_1 -like symmetry. The remaining peak at E_F has Λ_3 -symmetry and is due to emission from bulk d-bands.⁴ It should be noted that the selection rules in this form cannot be strictly applied to Ir(332) because of a lowering of the symmetry due both to the presence of steps and to relativistic effects.

Energy dispersions $E(k_{\parallel})$ of terrace- and step-related surface states perpendicular and parallel to the rows of step atoms (along the $[\bar{1}\bar{1}3]$ and $[\bar{1}\bar{1}0]$ directions respectively) are shown in Fig.2.¹² Both states have maximum intensity at the \bar{Y} point ($k_{\parallel} = 0.247\text{\AA}^{-1}$ along $[\bar{1}\bar{1}3]$) of the (332)-SBZ. The bulk band structure projected onto this value of k_{\parallel} contains the L point, around which a sp-hybridization gap is centered.⁴ The surface states are found to lie in this sp gap above the L_2' point (L_6 - in double group notation) and have maximum intensity for photon energies of ~ 8 to 10 eV, i.e., for values of perpendicular momentum k_{\perp} at which direct transitions take place into the nearly-free-electron sp-final band near the L point. In Fig.2, the parabolic curve through L_2' (and shaded region) roughly delineates the region in \vec{k} -space

for which Λ_1 -symmetry (Λ_6 - in double group notation) initial bulk bands exist. In fact, both states are surface resonances in a relative gap, since there exist bulk states of the same symmetry with the same k_{\parallel} values.⁴ As Fig.2 demonstrates, the step-related surface state does not show measurable dispersion, whereas the terrace-related state exhibits a dispersion similar to that for the Ir(111) surface state around the Γ point of the (111)-SBZ. The presence of steps introduces a slight anisotropy in the dispersion of the terrace-related state, corresponding to an effective mass ratio of $m^*_{\perp}/m^*_{\parallel} = 1.19$ (m_{\perp}^* (m_{\parallel}^*) is the effective mass as determined in a direction perpendicular (parallel) to the steps). We also note from Fig.2 (TER. + H/STEP) that the quenching of the step-related state by hydrogen adsorption is accompanied by a 0.1 eV lowering of the binding energy of the terrace-related state. It is further lowered in energy by 0.1 eV and partially quenched if the terrace sites are occupied by hydrogen. This behavior is similar to that reported for H on Ni(111)¹³ and indicates that sp-like surface states play a role in the bonding of H to Ir for low coverages.

Using step- and terrace-related surface states to delineate different adsorption sites, we have studied the catalytic reaction between hydrogen and pre-adsorbed oxygen at 300 K (Fig.3). Exposure of the clean surface (curve a) to 0.5 L of oxygen results in both step- and terrace-induced states being simultaneously quenched (curve b), indicating that oxygen readily adsorbs on both step and terrace sites. Upon exposure of the oxygen-saturated surface

(curve c) to hydrogen, both surface states were found to re-appear (curves d and e), because the hydrogen reacts with oxygen on both steps and terraces, resulting in the formation of water which subsequently desorbs. After 40 L of hydrogen some of the step sites become re-occupied by hydrogen, as is evident from the partial quenching of the step-related state (curve f). However, some oxygen is still left on the surface since the terrace-related state has not yet regained full strength. Upon heating to ~ 450 K in vacuo the oxygen and hydrogen atoms react to produce a clean surface (curve a).

Although it has long been assumed that metal surfaces interact with adsorbates such as H mainly via their d-orbitals,¹⁴ recent photoemission experiments^{13,15} and theoretical calculations¹⁶ have indicated the importance of substrate sp-orbitals for bonding in the system H on Ni. On the other hand, from photoemission measurements on Pd and Pt surfaces,^{15,17} it has been concluded that hydrogen chemisorption bonding to these heavier transition metals directly involves substrate d-electrons. The relative strength of sp-interactions versus d-interactions is not well known for these metals. Our results indicate that metal sp-electrons cannot be neglected in H bonding to Ir(332). In particular, the $\Lambda_1(s,p_z)$ -type step-related surface state near E_F is likely to contribute to the observed increase in the hydrogen chemisorption bond energy at the step sites.

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changes in the AREDC's are not due to the interaction of hydrogen with bulk d-bands.

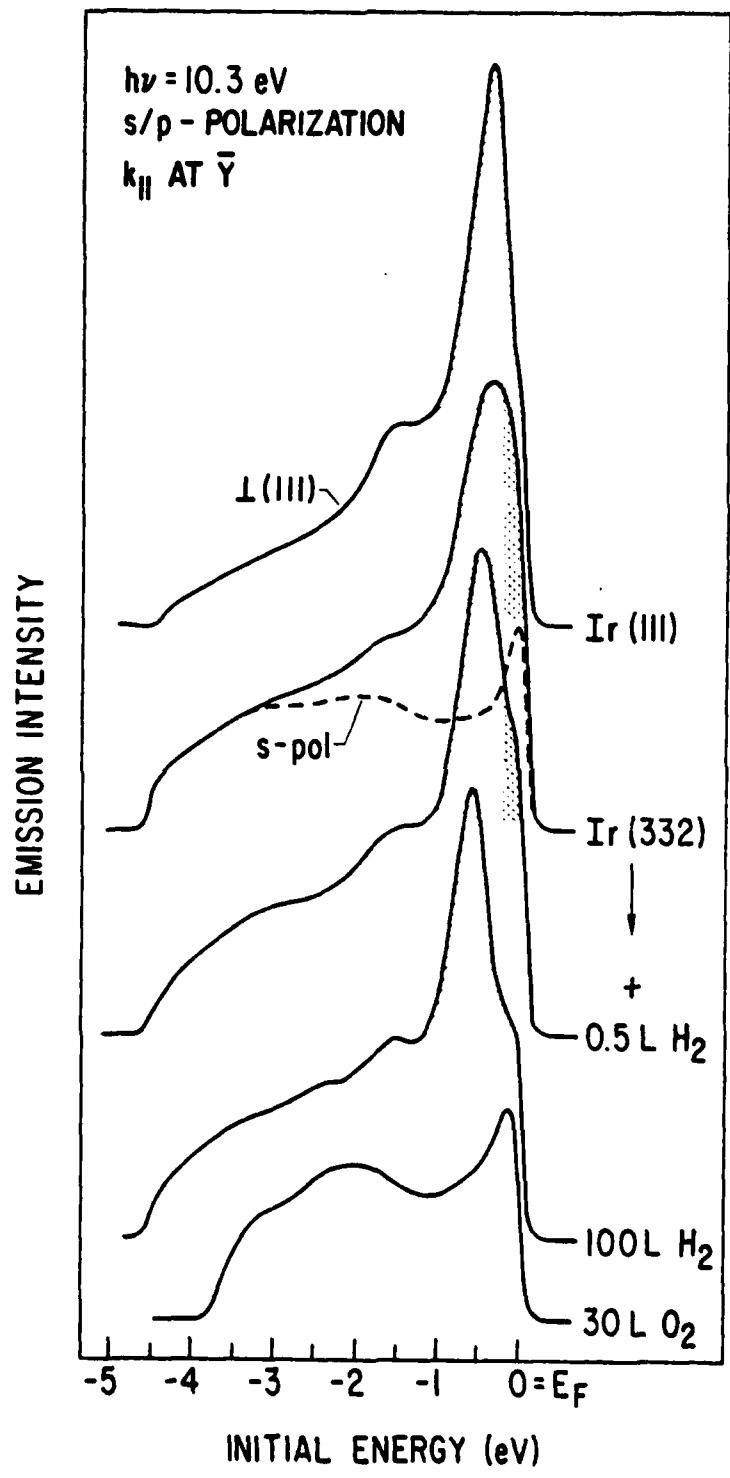
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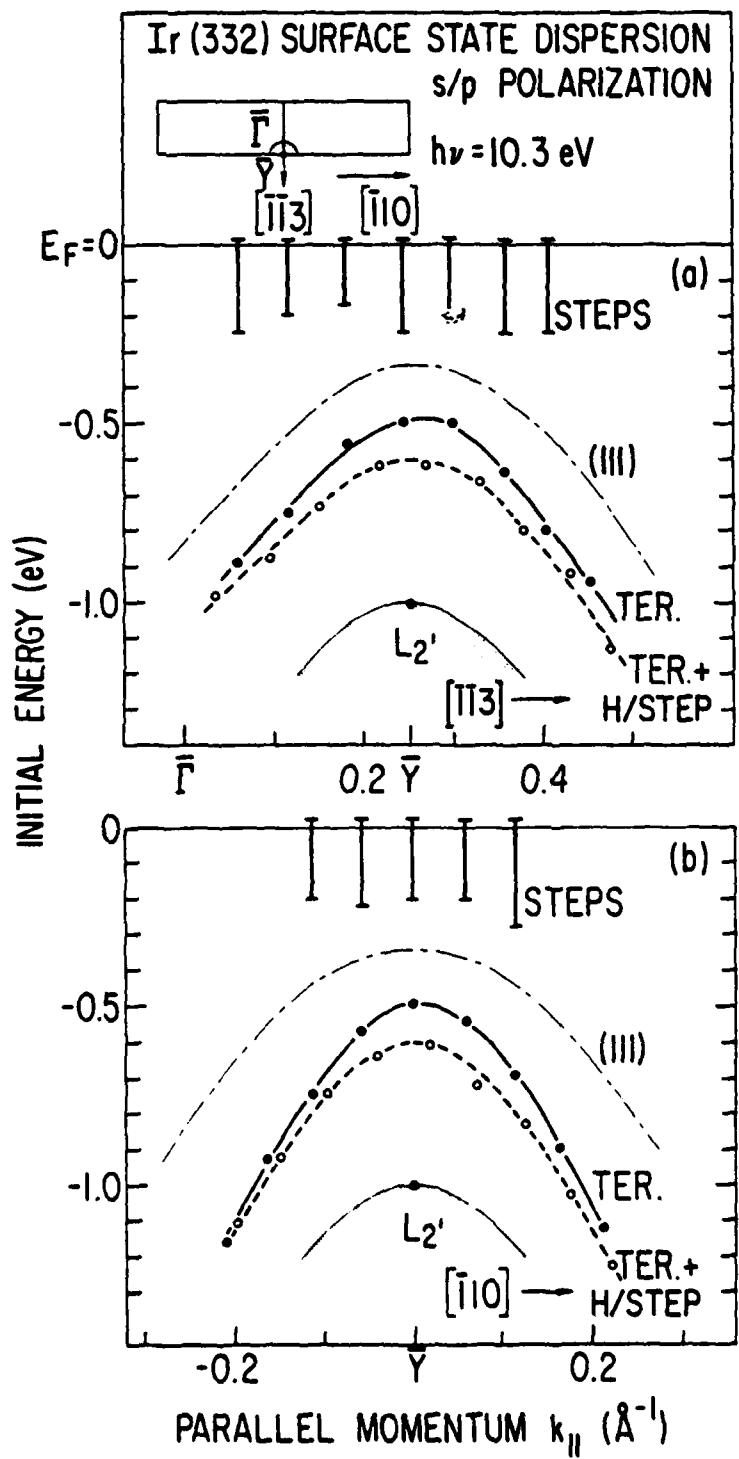
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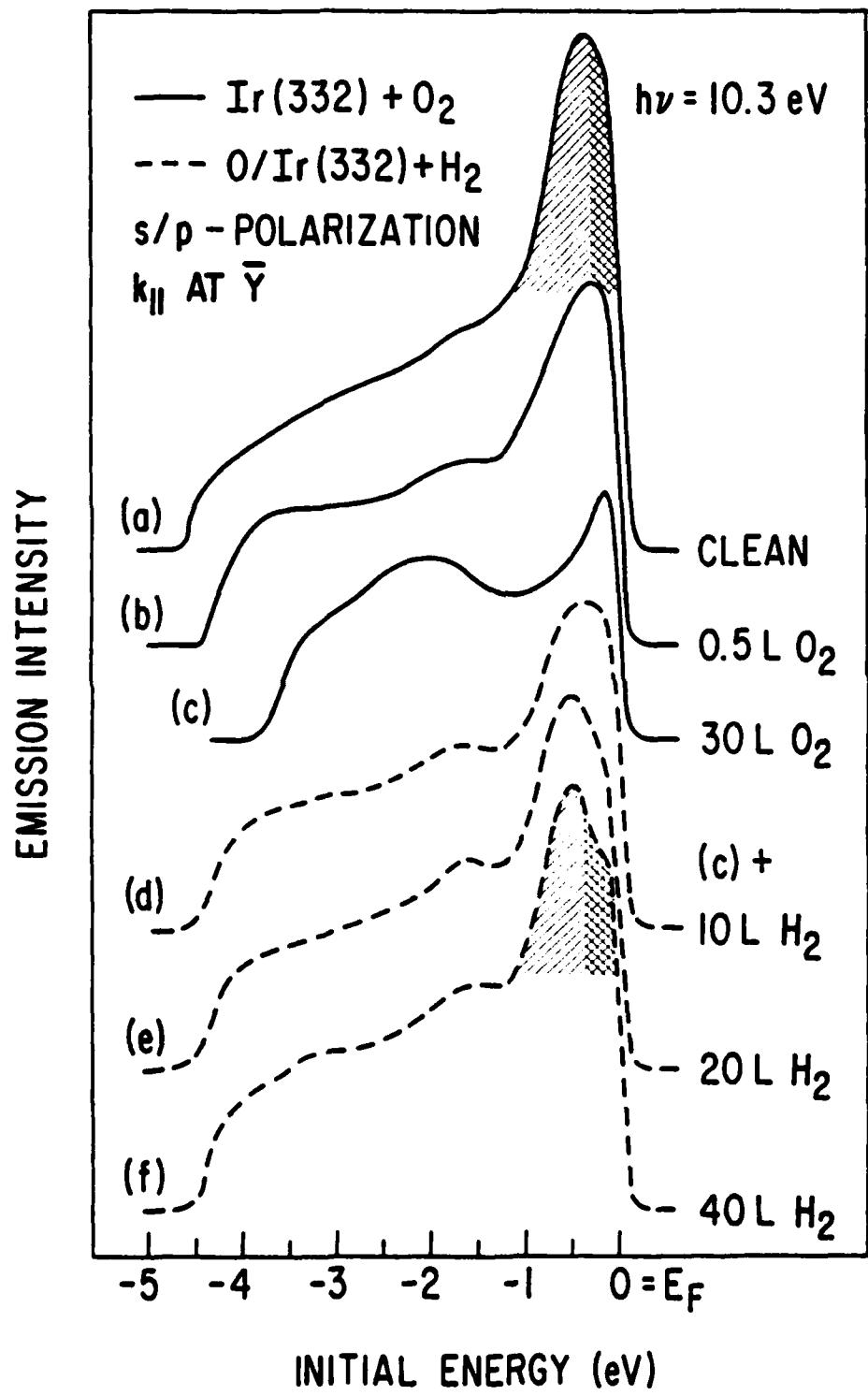
Fig.1 Angle-resolved electron energy distribution curves for Ir(332) and Ir(111) at $h\nu = 10.3$ eV. Single- and cross-hatched peaks are due to terrace- and step-related surface state emission.

Fig.2 Energy dispersion of surface states on Ir(332) and Ir(111). The insert at the top shows the (332)-surface Brillouin Zone (SBZ). Closed and open circles refer to the terrace-related state for clean and hydrogen-covered steps. The dispersion of the Ir(111) state around the Γ point of the (111)-SBZ is shown by the dash-dotted line.

Fig.3 Angle-resolved electron energy distribution curves for Ir(332) showing the effect of oxygen chemisorption and the H/O-catalytic reaction on step- and terrace-related surface state emission intensities.







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